END
DATE
FILMED

4 82

DTIC

1.0

1.1

1.25

2.8	2.5
3.2	2.2
36	
40	2.0
	1.8

1.4   1.6

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS 1963 A

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- **82 - 0 2 3 1**	2. GOVT ACCESSION NO. AD-A113067	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Interactions of Hydrazine and of Hydrazine Derivatives with Soil Constituents and with Soils		5. TYPE OF REPORT & PERIOD COVERED Annual Report – 01 Dec 80 – 01 Dec 81
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M.H.B. Hayes, P.J. Isaacson, K.Y. Chia, A.M. Lees		8. CONTRACT OR GRANT NUMBER(s) AFOSR-80-0032
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Birmingham Birmingham B152TT, U.K.		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2312/A5 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NL Bolling AFB, DC 20332		12. REPORT DATE 31 January 1982
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release;
distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hydrazines, Soil Adsorption, Degradation, Humic colloids, Homoionic Clays, Clay Colloids.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

(See Attachment)

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE   UNCLASSIFIED
1 JAN 73

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AFOSR-TR-82-0231

20. Abstract

Studies have demonstrated that at high pH, in the solution phase, colloids catalyse hydrazine degradation. This catalysis is particularly dependent upon the exchangeable metal cations held by the colloids, and exceeds that of equivalent solutions of the metal cations alone. Hydrazines can be strongly or weakly sorbed by soil colloids in essentially unchanged forms, or can be irreversibly chemisorbed. Reversible ion-exchange is the main mechanism of hydrazine/clay interaction at low pH. Insoluble iron-and aluminium-hydrous oxides form on the surfaces of suitably exchanged clays at high pH, and these bind large amounts of hydrazines by strong hydrogen-bonding forces and by hydrazination of cationic species. Such binding partially destabilises hydrazine towards thermal degradation. The results for synthetic goethites resemble those for iron(III) montmorillonite, but interactions are larger per gram of colloid. Reduction of iron(III) to iron(II) occurs, and an iron(II)/hydrazine coordination complex forms which deactivates surfaces at high pH, but is soluble at low pH. Hydrazines interact with humic colloids by chemisorption, by ion-exchange, and by hydrazination of strongly polarizing cations. The reactivity of humates is determined by their exchangeable metal cations, and by the pH, which both affect their penetrability and solubility. Clay colloids and goethite react strongly with hydrazines from the vapour phase. Results show that the hydrazines can compete well with water for interaction sites. The presence of water also determined the products of thermally induced degradation of sorbate molecules. Preliminary results from whole soil/hydrazine experiments show the large capacity of different soil types for interaction with hydrazines. A copper(II)-treated, aerated clay soil is highly effective in degrading applied hydrazine.

Uncl.

AFOSR-TR- 82-0231

EA ORD 81-093

INTERACTIONS OF HYDRAZINE AND OF HYDRAZINE

DERIVATIVES WITH SOIL CONSTITUENTS AND WITH SOILS

M.H.B. Hayes, P.J. Isaacson, K.Y. Chia, A.M. Lees,
Department of Chemistry,
University of Birmingham,
Birmingham.
B15 2TT
U.K.

31 January 1982

Annual Scientific Report   -   1 December 1980 – 1 December 1981

Prepared for

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

and

EUROPEAN OFFICE OF AEROSPACE RESEARCH AND DEVELOPMENT

London, England.

82 04 06 117

INTERACTIONS OF HYDRAZINE AND OF HYDRAZINE DERIVATIVES

WITH SOIL CONSTITUENTS AND WITH SOILS.

M.H.B. Hayes, P.J. Isaacson, K.Y. Chia, A.M. Lees.

Annual Scientific Report,   1 December 1980 - 1 December 1981

PREFACE

This report is of work carried out by members of the Soil Chemistry Section,
Department of Chemistry, University of Birmingham, Birmingham. B15 2TT, U.K.,
under contract from USAF (EAORD-81-093).

ABSTRACT

The results of studies are reported on:

a) the solution-phase interactions of hydrazines with homoionic clay and humic colloids, and with hydrous iron oxides;   b) the vapour-phase interaction of hydrazines with homoionic clays, and with hydroxy-aluminium coated clays;   c) the vapour-phase interaction of water with homoionic clays;   and d) hydrazine/whole soil interactions.

At high pH, in the solution phase, the colloids catalyse hydrazine degradation. This catalysis is particularly dependent upon the exchangeable metal cations held by the colloids, and exceeds that of equivalent solutions of the metal cations alone.

Hydrazines can also be strongly or weakly sorbed by soil colloids in essentially unchanged forms, or it can be irreversibly chemisorbed. Reversible ion-exchange is the main mechanism of hydrazine/clay interaction at low pH. Insoluble iron- and aluminium-hydrous oxides form on the surfaces of suitably exchanged clays at high pH, and these bind large amounts of hydrazines by strong hydrogen-bonding forces and by hydrazination of cationic species. Such binding partially destabilises hydrazine towards thermal degradation.

The results for synthetic goethites resemble those for iron(III) montmorillonite, but interactions are larger per gram of colloid. Reduction of iron(III) to iron(II) occurs, and an iron(II)/hydrazine coordination complex forms which deactivates surfaces at high pH, but is soluble at low pH.

Hydrazines interact with humic colloids by chemisorption, by ion-exchange, and by hydrazination of strongly polarizing cations. The reactivity of humates is determined by their exchangeable metal cations, and by the pH, which both affect their penetrability and solubility.

Clay colloids and goethite react strongly with hydrazines from the vapour phase. Hydrazine and water-vapour sorption are compared. Results show that the hydrazines can compete well with water for interaction sites. The presence of water also determines the products of thermally induced degradation of sorbate molecules.

Preliminary results from whole soil/hydrazine experiments show the large capacity of different soil types for interaction with hydrazines. A copper(II)-treated, aerated clay soil is highly effective in degrading applied hydrazine.

LIST OF CONTENTS

1. INTRODUCTION

The overall aims of the research project are to establish the extents to which hydrazine and methylhydrazine compounds interact with soil colloidal constituents, and to understand the mechanisms of the interactions. This is done so that plausible recommendations can be made for the minimization of the possible impact of hydrazine compounds on the soil environment, and for the reclamation of contaminated soils. The information obtained about the interactions also illustrates the fundamental chemical properties of the surfaces of the soil colloids.

The soil environment contains extensive active surfaces, a variety of metal ion species, and an inter-related liquid/vapour phase system within a matrix of solids. A large potential for interaction therefore exists under conditions of normal environmental temperature and pressure. The colloidal constituents are the active surfaces in soils in so far as interfacial reactions are concerned. These components are clays and clay-type minerals, various hydrous oxides of iron and aluminium, and the amorphous, organic humic colloids. Each may be present independently of the others in the soil, but more generally some or all are associated together to present a complex adsorbing surface. In order to understand the interactions between hydrazine sorptives and these complex soil colloids it has been considered appropriate to study the general types of reactions between hydrazines and well characterized preparations of clays from deposits, laboratory synthesized hydrous oxides of iron and aluminium, and fractionated humic colloids extracted from soils. Results obtained with isolated, natural soil components can then be compared with, and interpreted in the light of those from interactions of the model compounds.

It is important to carry out some studies with whole soils, in order to establish the relevance to field conditions of studies with model compounds and with isolated soil colloids. This work can be attempted in the laboratory by using soil columns to approximate to in situ soil cores.

A short summary is provided below of the results described in the First Annual Report (AFOSR-80-0032) (Hayes et al., 1980). This is followed by a detailed report of the results for December 1980 to November 1981, together with overall discussion and conclusions.

2. SUMMARY OF FIRST ANNUAL SCIENTIFIC REPORT

The results contained in the First Annual Scientific Report demonstrate that the colloidal components of soil have a large influence on the fate of hydrazines in the soil environment. This influence arises through two main effects, degradation and sorption.

Hydrazine degradation commonly occurs in solution above pH 7 in the presence of oxygen. A variety of clay colloid preparations all act as catalysts for this degradation, and they can give rise to four to five-fold increases in the extent of degradation over a five hour period. The type of clay mineral examined determines the extent of the catalytic effect, in that the greater the surface area of the clay mineral, and the greater its cation exchange capacity, the greater is the catalysis. However, the most marked catalytic influence is shown to be the particular cation associated with homoionic preparations of the clays. The effective concentration of the cation that is encountered by sorbed hydrazine molecules is higher than that found in the bulk solution, and sorbed hydrazines are held in close proximity to the exchangeable cations. These two factors greatly increase the likelihood of hydrazine/metal/oxygen interactions, which may lead to degradation. Smectite-type clays exchanged with copper(II) ions are the most effective catalysts of the soil colloids examined.

All the clays, synthetic hydrous oxides, and humic materials examined are shown to sorb hydrazines. Some strong, irreversible sorption occurs in some instances, but in general the sorption is reversible. The properties of the medium that determine the extent of sorption are shown to be the solution pH, and the exchangeable metal cations held by the clay and humic colloids, or the metal of the hydrous oxide colloids.

The pH values of the natural soil solution of most agricultural soils are in the range of 4-8, and these are the extremes of solution pH examined. The interaction mechanisms in low pH systems are shown to be relatively simple, and to be dominated by reversible hydrazinium/cation exchange processes. Indeed cation exchange is the main process of interaction with monovalent cation-exchanged clays at all pH values. Hence, the extent of adsorption decreases as the extent of protonation of the hydrazines decreases. The amount of surface available for coverage on different clay types also determines the extent of sorption.

Preliminary results show that sorption of hydrazine by humic polymers at low pH is affected by the penetrability of the polymers, and this varies with the exchangeable cation.

At high pH the polymers go into solution as flexible, loosely coiled forms, and their penetrability becomes more uniform. The main mechanisms of sorption of the hydrazines by humic polymers are cation exchange, and chemisorption by condensation with carbonyl groups in the humic molecules.

Iron, manganese, and aluminium-exchanged clays have enhanced interactions with hydrazines at high pH, where conditions are such that insoluble hydroxides of these metals form. These effects are larger than for equivalent solutions of the metal species alone. The extent of interaction of hydrazine with synthetic hydrated iron oxide is also large at high pH, but the interaction is complicated at low pH by the possible solubilization of a hydrazine hydrochloride/ferrous iron complex.

Adsorption of vapour phase hydrazines by soils can be important, especially in the cases of soils in the neighbourhood of spills. Hydrazines are shown to be readily sorbed from the vapour phase by homoionic clay preparations and by soil clays. Irreversible sorption is greater for smectite-type than for kaolinitic clay minerals, and is also enhanced by the presence of organic matter intimately associated with the clay, and by the presence iron(III) as the exchangeable cation.

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 First Annual Scientific Report

Samples of the model colloids were prepared by the methods described in the First Annual Scientific Report.

3.1.2 Soils

Three soils of different textural classes were sampled from their surface horizons, and the samples were air-dried and sieved to obtain the < 3.38 mm fraction. The three soils were a clay loam (Highweek Series, Major Soil Group - Brown Earth), a sandy loam (Bridgnorth Series, Major Soil Group - Brown Earth), and a loam (Crediton Series, Major Soil Group - Brown Earth) (Memoirs of the Soil Survey of England and Wales).

3.1.3 Preparation of aluminium hydroxy montmorillonite

Sodium hydroxide solution (0.1 M) was added slowly by use of a syringe to a 0.5% w/v suspens .n of alu. .um-exchanged montmorillonite. The suspension was thoroughly mixed

after each small addition until a steady pH was registered. Further sodium hydroxide solution was added until a final pH of 8 was obtained. The suspension was allowed to stand overnight. Fresh material was prepared for each experiment.

3.2 Methods

3.2.1 First Annual Scientific Report

The First Annual Scientific Report contains details of the methods used to quantitate hydrazine and monomethylhydrazine, and to determine sorption and desorption isotherms from solution by a continuous-flow stirred cell technique, and from the vapour phase by a gravimetric technique. The Report also describes the microcalorimetric method used to measure heats of reaction of solution phase interactions.

3.2.2 Determination of iron

Iron was determined by a standard method (Belcher and Nutten, 1970) involving formation of an iron-thiocyanate complex. Iron(II), if present, was oxidized to iron(III) with 20 volume hydrogen peroxide in trichloroacetic acid, and the total iron(III) was reacted with 1 $\underline{M}$ sodium thiocyanate solution. The absorbance of the pink complex formed was measured at 455 nm immediately after mixing.

3.2.3 Self-supporting clay films

Self-supporting clay films for infra-red spectroscopy were prepared by the suction of 20 cm^3 of 0.5% w/v clay suspension through a 0.01 µm cellulose nitrate membrane filter (Sartorius Instruments Ltd., Surrey, England). The filter and clay film was then placed in an open oven to dry at 80°C, after which the approximately 20 µm thick clay films could be peeled intact from the filter.

3.2.4 Infra-red spectroscopy

Infra-red spectra were recorded using a Perkin Elmer 180 spectrometer, over the range 500 to 4000 cm^{-1}.

3.2.5 Differential thermal analysis

Thermograms were obtained in a nitrogen atmosphere using a Stanton Redcroft Thermal Analyser STA 780, over the range 25 to 400°C, with temperature programming at 4°C min^{-1}.

3.2.6 Mössbauer spectroscopy

Mössbauer spectra were obtained using a Cryophysics MS-102 Microprocessor Mössbauer Spectrometer, using a ^{57}Co source.

3.2.7 X-ray diffractometry

A Phillips PW 1050/70 Diffractometer was used to examine clay and hydrous oxide samples before and after sorption of hydrazines from the vapour and solution phases. Some clay samples were examined as wet slurries (Pick, 1973).

3.2.8 Whole soil columns

The seived (< 3.38 mm), air-dried, soil was mixed with an equal weight of fused alumina anti-bumping granules (Fisons Scientific Apparatus, Loughborough, England), and placed over a sintered glass disc in a 15 cm glass column (4 cm i.d.), and covered with 1 cm depth of anti-bumping granules (Figure 1). A three-port glass cap was fitted and sealed in place by an inert "O"-ring. The soil was first flushed with nitrogen (anaerobic experiment) or air (aerobic experiment), then washed with de-aerated or aerated water by pumping into the input port. This was followed by the solutions relevant to the experiment. The gas inlet and outlet ports allow an atmosphere of known composition to be maintained, and also allow collection of volatile products.
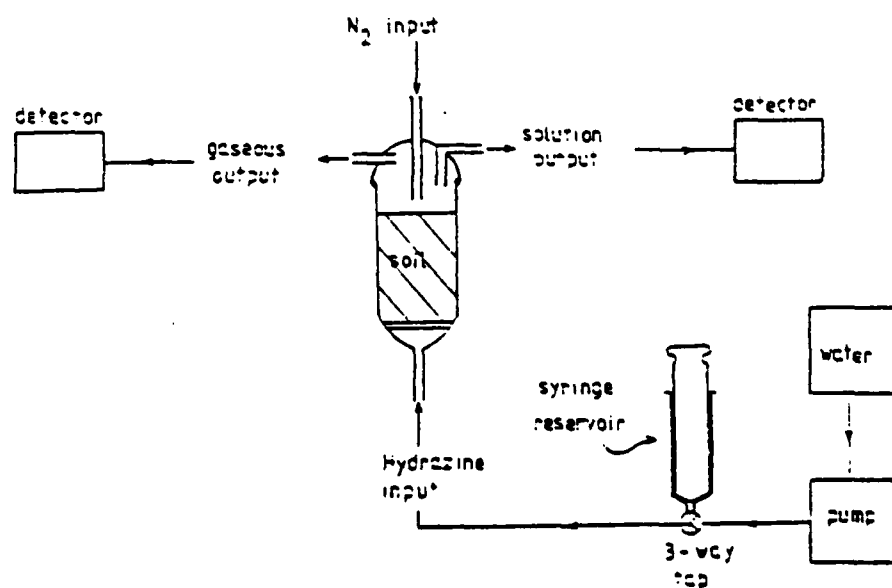

Figure 1. Schematic diagram of sorption apparatus for whole-soil experiments.

4. RESULTS AND DISCUSSION

4.1 Solution Phase

4.1.1 Catalysis of hydrazine degradation

Some of the results contained in the First Annual Scientific Report are included in this section to give an overall description of the catalytic effect of the model colloids.

All the soil colloids catalysed the degradation of hydrazines in solution at pH values greater than 7, and in the presence of oxygen. Experiments performed with hydrazine hydrate solutions were repeated for monomethylhydrazine solutions, and the results were essentially the same. Results obtained with hydrazine solutions and some of the colloids are used to illustrate the overall behaviour.

The amount degraded (Figure 2) over a 5 h period at pH 8 decreased in the order copper(II) montmorillonite ($>$ 90%), goethite (50%), iron(III) montmorillonite (50%), aluminium montmorillonite (35%), iron(III) humate (30%), sodium montmorillonite (25%), sodium kaolinite (15%), no sorbent ($\sim$10%). In every case the amount degraded was greater than observed for solutions of the metal chlorides at the same metal ion concentrations (not applicable for goethite).
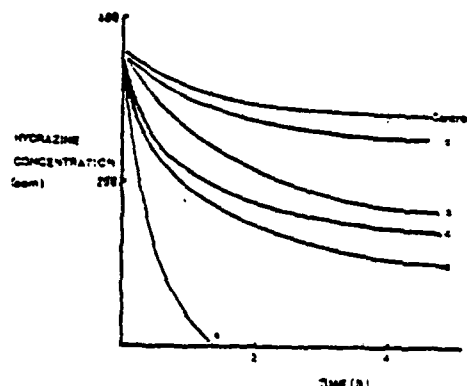

Figure 2. Catalysis of hydrazine degradation by:

    a)   sodium kaolinite
    b)   sodium montmorillonite
    c)   aluminium montmoriilonite, iron(III) humate
    d)   iron(III) montmorillonite, goethite
    e)   copper(II) montmorillonite

The results show that the exchangeable metal cation is the major factor which determines the magnitude of degradation catalysis; e.g. copper(II) montmorillonite is three times more effective than sodium montmorillonite. Transition metals are able to act as one- or two-election acceptors (Bottomley, 1970), and to react with hydrazines in the absence of oxygen. However, sodium-exchanged clays gave no degradation at pH 8 when oxygen-free solutions were used. The effect of the colloids themselves depended on their surface characteristics, and their abilities, if any, to react chemically with hydrazines. Montmorillonite (expanding layer), and illite (non expanding) have significantly greater surface areas and cation exchange capacities (CECs) than kaolinite (Greenland and Mott, 1978). This is reflected in the ability of sodium montmorillonite (CEC 0.80 meq g^{-1}) to degrade twice as much hydrazine as sodium kaolinite (CEC 0.10 meq g^{-1}), and to irreversibly bind some sorptive. The behaviour of goethite resembles that of iron(III) montmorillonite (Figure 2), showing that the clay is effectively presenting a hydrous oxide surface for hydrazine interaction. It must also indicate that the surface of the hydrous iron oxide is inactivated during reaction (Section 4.1.2.2), rather than the iron/hydrazine reaction proceeding to complete reduction of available iron(III). The interaction with humic materials is complicated by the ability of the sorbent to irreversbily chemisorb hydrazines (Section 4.1.2.3), and to form strong chelate complexes with metals such as iron and copper (and thereby to restrict their catalytic action (von Aebi et al., 1965)).

The method used to measure hydrazine concentrations of solutions would also semi-quantitatively measure sorbed hydrazines if it was applied to hydrazine/colloid suspensions. The hydrazine concentrations of all the colloid suspensions (humic acids are soluble at pH 8) were greater than those of the supernatants. Some hydrazine was even sorbed undegraded by copper(II) montmorillonite after 5 h. The two processes of sorption and degradation occur together, and it is reasonble to assume that sorption precedes colloid catalysed degradation. To an extent a distinction can be made between the two processes by carrying out experiments in the absence of oxygen, and by determining how much hydrazine can be desorbed unchanged after interaction. The reactions between metals and hydrazines are energetically favourable, and the limiting process in colloid catalysed degradation is likely to be the extent to which any of the possible sorption processes take place.

The degradation of hydrazine during its passage through untreated, and copper(II)-treated whole soil columns is described in Section 4.3.1. The thermally induced

degradation of hydrazine sorbed by aluminium-hydroxy montmorillonite is described in Section 4.1.2.2 (solution-phase complexes), and Section 4.2.2 (vapour-phase complexes).

4.1.2 Sorption processes

The solution pH determines the type and extent of interaction that can occur between hydrazines and a given colloid exchanged with a particular metal cation, or between hydrazines and an hydrated iron oxide. Oxygen-free systems were examined using the continuous-flow method (Section 3.2.1). The behaviour of the systems at pH 4 and pH 8 were examined, since these are the extremes of pH that may normally be expected to occur in soils.

4.1.2.1 Clay colloids

The First Annual Scientific Report contains results of microcalorimetry and sorption experiments using a number of clay minerals exchanged with sodium, potassium, calcium, manganese(II), copper(II), aluminium(III), and iron(III) metal cations.

4.1.2.2 Hydroxy-aluminium montmorillonite

Experiments described in the First Annual Scientific Report showed that extensive and energetic sorption occurred when hydrazine solution was mixed with suspensions of iron(III)- or aluminium(III)-exchanged montmorillonite suspensions. Much more extensive sorption occurred at high pH than at low pH, which is of particular interest because any introduction of hydrazine into a soil system will tend to increase the pH of the soil solution.

Hydrous oxides of iron and aluminium are insoluble at high pH, and these can form either as discrete precipitates, or as "films" on the colloid surfaces. The formation of films will be favoured when the metal ions are already present on the colloid surfaces as the exchangeable cations.

Hydroxy-aluminium montmorillonite was prepared (Section 3.1.2) such that the clay had a partial coating of hydrous aluminium oxide, to the extent of the available aluminium. None of the aluminium in this clay preparation was exchangeable with sodium ions from a 0.1 $\underline{M}$ sodium chloride solution which had been adjusted to pH 8. A similar sample of hydroxy-aluminium montmorillonite was prepared using radioactive [22]Na-labelled sodium hydroxide solution, and this was found to have a sodium content slightly in excess of the CEC (0.95 meq g^{-1} at pH 4) of the untreated aluminium-exchanged

montmorillonite. Almost all the aluminium in the high pH-treated clay complex is therefore non-exchangeable, and is held in uncharged hydroxy-aluminium complexes, which will be distributed over the internal and external surfaces of the montmorillonite. The surface negative charges of this clay preparation are balanced by exchangeable sodium ions.

The interaction of hydrazine or monomethylhydrazine with the hydroxy-aluminium clay resulted in sorption described by high-affinity isotherms (Figure 3). In each case, all but 0.05 meq sodium per gram of clay was desorbed from the clay, but no aluminium could be detected in the supernatant solutions. The amounts of hydrazine (1.50 meq g^{-1}) and of monomethylhydrazine (2.00 meq g^{-1}) sorbed by the clay preparation were both well in excess of its CEC, and a large proportion of the sorbate could be desorbed by suspension of the hydrazine-clay complex in 0.1 $\underline{M}$ sodium chloride solution.
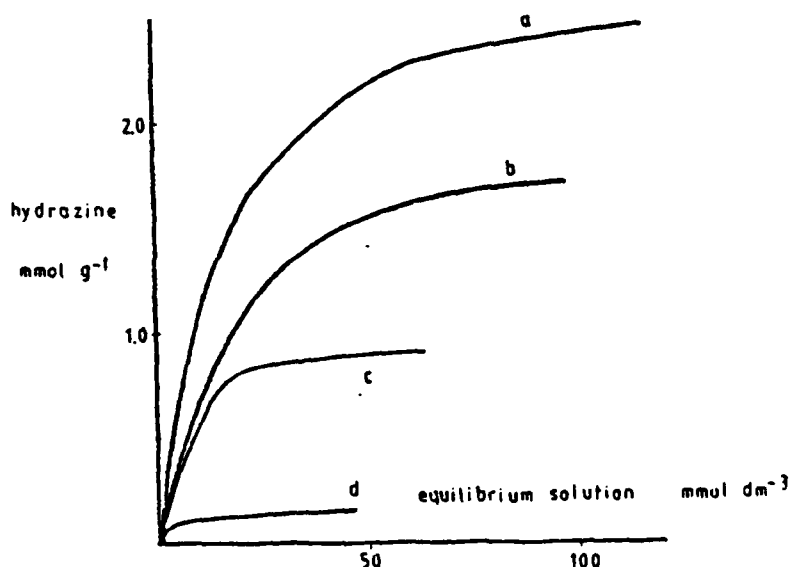

Figure 3.   Isotherms for the sorption of a) monomethylhydrazine by hydroxy-aluminium montmorillonite at pH 8, and of hydrazine by hydroxy-aluminium montmorillonite at b) pH 8,   c) pH 4,   and d) unadjusted pH.

The pka value of hydrazine (8.07 at $30°C$), and for monomethylhydrazine (7.87 at $30°C$; Hinman, 1958), are such that a significant proportion of both hydrazines will be protonated at pH 8 in the bulk solution. This proportion will be even greater near the clay surface, where the pH may be 2 to 4 pH units lower than in the bulk solution (Bailey et al., 1968) due to partial dissociation of hydroxyl groups of the aluminium hydroxy complexes to yield acidic protons.

Infra-red spectra of the complexes formed between either hydrazine or monomethyl-hydrazine and the hydroxy-aluminium complex show a high degree of polarization of most

N-H bonds in the sorbate molecules (Chia et al., 1982). The results show that the hydrazines are sorbed by exchange with sodium cations, and by protonation at acidic hydroxyl sites. A further binding mechanism is the displacement of cation-solvating water by the strongly nucleophilic hydrazines.

Infra-red spectra of the solution-phase hydrazine-, and monomethylhydrazine complexes with the hydroxy-aluminium clay clearly show that heating the complexes to 110°C results in partial degradation of the sorbate molecules. The major product of degradation is ammonia, which is also strongly sorbed by the clay preparation.

An interesting indication of the infra-red spectra is that monomethylhydrazine sorbed by the clay preparation acts as a slightly stronger base than hydrazine although in solution it is a slightly weaker one. The clay sorbs a third more monomethylhydrazine than hydrazine, and hence the monomethylhydrazine causes a greater displacement of interlayer water, and subsequently a greater enhancement of the acidity of the remaining interlayer water (Heller-Kallai et al., 1973). This enhancement is shown by an intensification of the polarization of N-H and O-H bonds in the monomethylhydrazine-hydroxy aluminium montmorillonite complex.

Differential thermal analysis of the solution-phase complexes showed that the sorbed hydrazines degraded by two mechanisms, and that these degradations occurred at 230 and 350°C.

The differential thermograms for either the hydrazine, or the monomethylhydrazine complexes were similar (Figure 4), and showed two exothermic, and one endothermic, responses under a nitrogen atmosphere. In an air atmosphere all three responses were exothermic.

Figure 4. Differential Thermal Analysis response of hydrazine treated hydroxy-aluminium montmorillonite.

The broad exothermic response centred at 65°C (Figure 4) in the thermograms is due to dehydration of the clay complexes. Three possibilities exist for unimolecular decomposition of hydrazines that could correspond to the other two responses; these are N-N homolysis, four-centre concerted loss of ammonia, and four-centre concerted loss of molecular hydrogen (Golden et al., 1972). The observed heats of reaction obtained from the thermograms (Table 1) for the endothermic response (at 350°C), can be compared with those quoted for the four-centre concerted loss of molecular hydrogen, which are 115 and 86 kJ mol^{-1} endothermic, respectively, for hydrazine and monomethylhydrazine (Shaw, 1975), and the agreement is good for the hydrazine sorbate.

TABLE 1

Heats of Reaction from Differential Thermograms of
Hydroxy-Aluminium Montmorillonite Complexes

Sorbate	Exothermic Response (kJ mol^{-1})	Endothermic Response (kJ mol^{-1})
Hydrazine	-215	116
Monomethylhydrazine	-310	150

The transformation of the endothermic response to an exothermic one in the presence of air may result from the formation of water from the molecular hydrogen from decomposition, and oxygen from the atmosphere.

The heats of reaction for the exothermic response at 230°C are larger than those reported for four-centred loss of ammonia, and are of the same magnitude as the N-N bond strengths of the two hydrazines (Shaw, 1975). However, the infra-red evidence for production of ammonia during decomposition shows that this is the main mechanism operating up to 250°C (see above). If the four-centre concerted loss of ammonia is the process for generation of the ammonia, then it is obvious that sorption of the hydrazines has considerably lowered activation energy barriers for this process.

It is interesting to note that the endothermic response at 350°C was observed even if the hydrazine-clay complex was maintained at 230°C for a prolonged period, before further heating to 350°C. A fraction of the sorbed hydrazines were held, therefore,

in such a way that they were resistant to decomposition at the lower temperature.

The direct treatment of an aluminium(III) montmorillonite suspension (pH 3.6) with hydrazine or monomethylhydrazine solutions (to give final pH 8) gave isotherms similar to those for the pre-treated clay, but with less extensive interaction (Figure 3). This shows the less extensive development of the hydroxy-aluminium polymers under these conditions. Similar direct treatment of an iron(III) montmorillonite suspension gave more extensive interaction (0.10 meq g^{-1}) than the aluminium-exchanged clay, but the interaction was increased even further by clay pre-treatment at pH 8. An extensive examination of the hydroxy-iron montmorillonite performance is being performed in the light of the results from the hydroxy-aluminium clay complexes.

4.1.2.3 Hydrous oxides

Isotherms, at pH 8, 7, and 4, for the interaction of goethite (hydrated iron oxide) with hydrazine are shown in Figure 5. The very strong interaction at pH 8 (up to 6.4 meq g^{-1}) exceeds that of any of the other colloids examined.
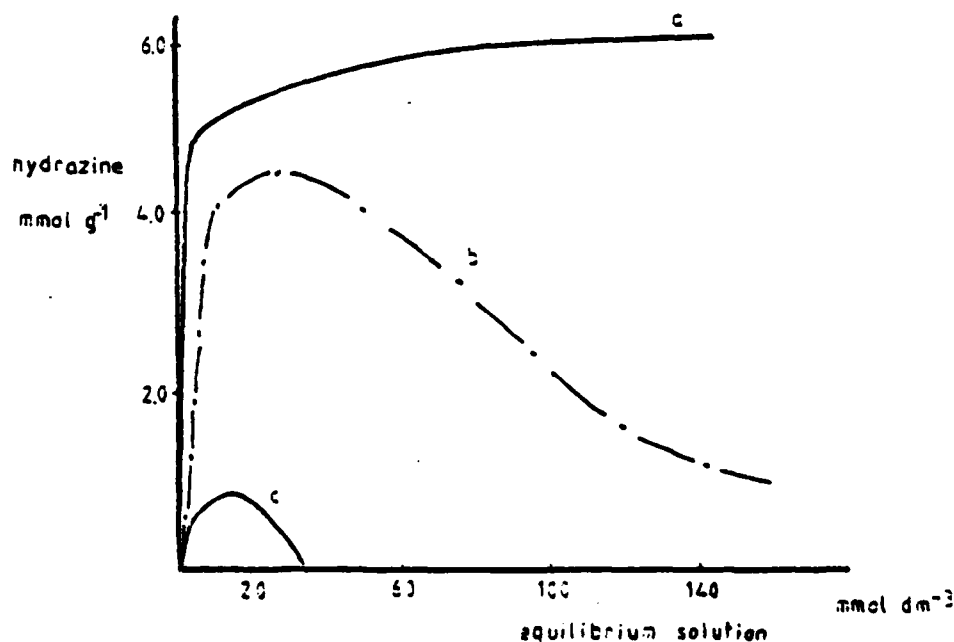
Figure 5. Isotherms for the sorption of hydrazine by goethite at:
a) pH 8, b) pH 7, and c) pH 4.

· The shapes of isotherms b and c in Figure 5 are due to excessive loss of hydrazine from the continuous-flow stirred cell during the progress of sorption experiments at pH 7 and 4. Analysis of the eluate from the flow cell showed that it contained iron(II), but no iron(III). The release of ferrous iron began as soon as hydrazine entered the flow cell at pH 4 and 7, and the rate of release rose rapidly to a maximum in a few minutes, then slowly decreased

as fresh hydrazine was supplied from the system reservoir. No ferrous iron was eluted from goethite contained in the flow cell when this was treated with a Tris(trihydroxymethyl-methylamine)/hydrochloric acid solution at pH 4. The implication of these observations is that hydrazine reacts with goethite in anaerobic suspension to produce some ferrous iron, which then forms a complex with further hydrazine. This complex is soluble at low pH, and passes through the membrane of the continuous-flow cell.

The low pH eluate from the flow cell was collected and freeze dried, to give an off-white, crystalline solid containing iron(II), hydrazine, and chloride (from the hydrochloric acid used to lower the pH of the hydrazine solutions). Differential thermal analysis of this solid showed that it melted at 82°C, and decomposed violently at 400°C, giving off ammonium chloride and leaving an off-white, non-magnetic ash. The iron(II) hydrazine complex was therefore masked by a large excess of hydrazine hydrochloride.

The fact that the goethite/hydrazine isotherm at pH 8 reached a plateau (Figure 5a), shows that the continued addition of hydrazine at this pH did not progressively consume the goethite. No ferrous iron was detected in the cell eluate. The surface of the colloid must therefore have become saturated with sorbed hydrazine, or inactivated by coverage with the iron(II) hydrazine complex which is insoluble at this pH. The complex $Fe(N_2H_4)_2Cl_2$ was prepared (Franzen and von Mayer, 1908) for X-ray comparison with the interacted goethite. Though the goethite diffractogram showed the presence of several phases after interaction, this cannot yet be identified.

Mössbauer spectra of the interacted goethite do not show the presence of iron(II), due to oxidation of the sample during the recording of the spectra. The technique of sample handling is being modified to prevent access of oxygen to the complexes.

Differential thermal analysis of the interaction complex shows only that goethite is transformed to haematite on heating, by dehydration at 250°C.
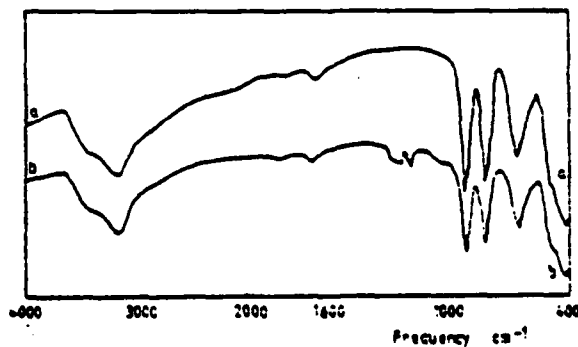

Figure 6.   Infra-red spectra of a) goethite, and b) water-washed hydrazine/goethite complex prepared from the solution phase.

The infra-red spectrum of the water-washed complex formed between hydrazine and goethite at pH 8 (Figure 6), shows absorption peaks at 1150 cm^{-1} and 1230 cm^{-1} (broad) which are assigned to NH_2 deformation vibrations of hydrazine directly coordinated to iron (presumably iron(II)). The spectrum does not give any indication of other forms of hydrazine (e.g. protonated, hydrogen bonded) sorbed on the goethite surface, nor does it show the presence of ammonia from hydrazine degradation. The inference to be drawn is that the reaction of goethite with hydrazine at high pH involves the reduction of a certain fraction of ferric iron at the colloid surface. This reduction involves the oxidation, and hence degradation, of hydrazine. Further hydrazine molecules then complex with ferrous iron, which they may do by acting as uni- or bi-dentate ligands, or by forming bridging complexes which extend as infinite two dimensional chains (Bottomley, 1970). The complex formed is insoluble and precipitates on the colloid surface, thus inactivating it for further interaction.

Preliminary experiments to study the interaction of goethite with vapour-phase hydrazines are reported below (Section 4.2.3).

Goethite samples have been prepared with partial isomorphous substitution of 5, 10, 15, 20, 25, and 30 per cent aluminium for iron. These are likely to provide a major source of interactions with hydrazine in many soil types.

An unsuccessful attempt was made to synthesize ^{57}Fe-labelled goethite using $^{57}Fe(III)Cl_3$. The preparation of unlabelled goethite proceeds from $Fe(III) (NO_3)_3$ or $Fe(II)Cl_2$ solutions, and the incorporation of only very small amounts of the ferric chloride resulted in the more stable haematite form of ferric oxide being produced.

4.1.2.4 Humic colloids

Experiments to study the interaction of hydrazine and humic colloids, described in the First Annual Scientific Report, only used low sorptive concentrations. The continuous-flow apparatus has been subsequently modified to allow the use of hydrazine solutions up to 200 mmol dm^{-3} in concentration, and the interaction of these with hydrogen-, calcium-, copper(II)-, aluminium-, and iron(III)-exchanged humates have been examined in detail (Isaacson and Hayes, 1982).

Humic polymers become more and more soluble in aqueous systems as the pH rises from pH 3.5, so that continuous-flow experiments could only be carried out at pH 4. Differences in the reactivity of different humate preparations at this pH are partially

related to the rigidity and penetrability of the polymer molecules, and this will to some extent reflect the character of humic coatings of other soil colloids.
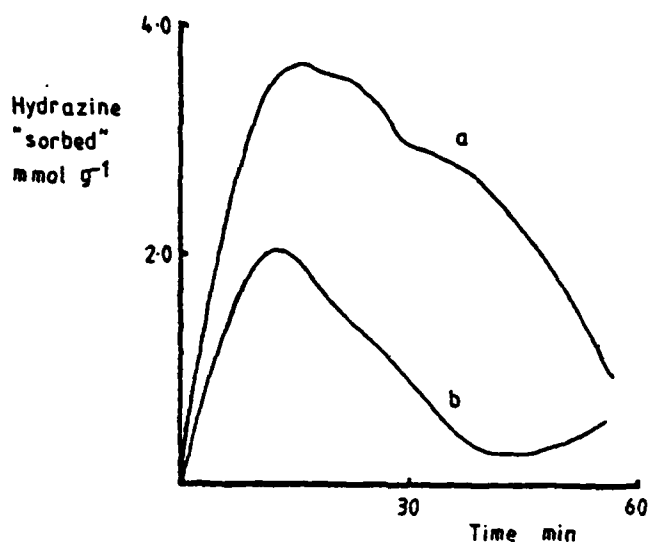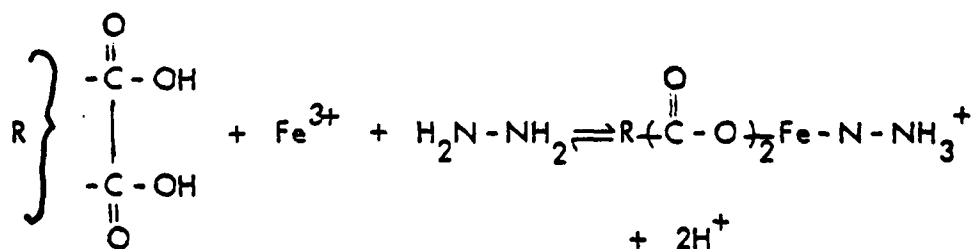

Figure 7. "Isotherms" for the sorption of hydrazine by: a) copper(II)-, and b) iron(III)-exchanged humate.

Isotherms for the interactions of hydrazine with the copper(II)-, and iron(III)-humate preparations are shown in Figure 7. Soluble reduced metal hydrazine complexes are formed in both cases, and hence the results from numerical analysis of the continuous-flow data do not yield true isotherms. However, considerable interaction occurs, and three possible types of interaction between hydrazine and iron(III) humate have been postulated (Griffith et al., 1980). Hydrazinium exchange with carboxyl protons, and complex formation with reduced iron may be accompanied by the formation of an organic salt or monodentate complex.

$$R \left\{ \begin{array}{c} \overset{O}{\underset{||}{}} \\ -C-OH \\ | \\ -C-OH \\ \underset{||}{} \\ O \end{array} \right. + Fe^{3+} + H_2N-NH_2 \rightleftharpoons R(\overset{O}{\underset{||}{C}}-O)_2 Fe-N-NH_3^{+} $$
$$+ 2H^{+}$$

where R represents the residual of the molecule in the humic materials. In the context of the last of these mechanisms, it is interesting to note that no more than two thirds of the exchangeable iron(III) of the humic colloid can be eluted from the flow cell as iron(II),

and no iron(III) is detected in the eluate. A further mechanism of interaction is by condensation of hydrazine with carbonyl groups on the humic molecules (see below).

Isotherms for the interaction of hydrazine with hydrogen-, calcium-, and aluminium-exchanged humate preparations are very similar to each other, and are of the high affinity type reaching plateaux at high equilibrium solution concentrations of hydrazine. The total amounts of hydrazine sorbed by the hydrogen-, calcium-, and aluminium-preparations respectively are 2.5, 2.3, and 2.0 meq g^{-1}. About 0.4 meq g^{-1} of hydrazine can be desorbed by washing with water in each case, and washing with 0.1 M sodium chloride solution desorbs 1.0, 1.0, and 0.9 meq g^{-1} respectively. The increase in nitrogen contents of the washed residues corresponds to 0.7, 0.6 and 0.4 meq g^{-1} irreversibly sorbed hydrazine.

The sorption isotherms have been analysed by a number of equations that have been used in soil science to describe sorbing systems. These equations were fitted to progressively larger ranges of each isotherm, to see if the "goodness-of-fit" varied as a function of the extent of the interaction examined.

The concentration of calcium (as measured by flame photometry) in the eluate from the calcium humate/hydrazine system shows a gradual desorption of the cation, as it is exchanged by hydrazinium ions. By contrast, no aluminium is desorbed from the aluminium humate system. (The maintenance of constant pH precluded the measurement of exchanged protons from the hydrogen humate).

The variations of the measured differential enthalpies of interaction (ΔH) are shown in Fig. 8, as a function of the equilibrium solution hydrazine concentration. All the interactions are exothermic, but the variation of ΔH is markedly different for the different humates. The ΔH value decreased for both the hydrogen-, and aluminium-humate interactions, but the initial increase was much sharper for the aluminium system than for the hydrogen humate. By contrast, the ΔH value for the calcium humate interaction increased with the extent of interaction.
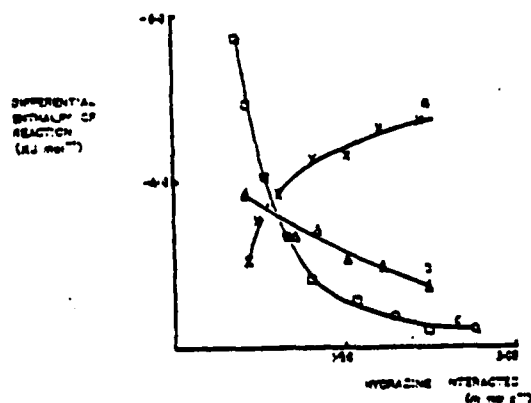

Figure 8. Variation of the differential enthalpy of reaction for the interaction of hydrazine

Infra-red spectra of the interaction complexes all show a marked decrease in absorption in the region 1690 to 1720 cm^{-1} (ketonic and carboxylic carbonyl), an increase in the region 1600 to 1640 cm^{-1} (C=N, C=O, C=C), and the appearance of shoulders at 3250 and 3310 cm^{-1} (N-H). This, together with elemental analyses, shows chemisorption of hydrazine by condensation with carbonyl groups to be one of the mechanisms of interaction. The nucleophilic character of hydrazine will also enable it to attack positions apart from, but activated by, carbonyl groups. Thus isoflavone and quinone structures in the humic materials will have resulted indirectly in the incorporation of some hydrazine.

The ability of sodium chloride solution to desorb unaltered hydrazine from the humic preparations shows that a large part of the hydrazine was held in the form of ionic complexes. Hydrazine in the form of hydrazinium cations is able to exchange for about a tenth of the calcium cations on the particular humic preparation. However, its inability to exchange for aluminium cations on humate structures, implies that salt-desorbable hydrazine in this case is originally held in the solvation shells of the carboxylate anions, by strong hydroxy bonding forces.

The differences in sorption behaviour of these three preparations illustrate the dramatic influence that the exchangeable cation can have on the properties of humic materials. All these materials were freeze-dried prior to preparation as suspensions for continuous-flow experiments, and this treatment enhances the tendency of humic polymers to associate, through polymer conformations in which these groups are preferentially orientated towards the "interior" of the randomly coiled polymers (Burchill et al., 1981). Such conformations are stabilized by strong intramolecular hydrogen bonds, which confer considerable rigidity on the humic structures, and this rigidity hinders the diffusion of sorptive into the "interior" of the molecule, where most of the binding sites will be located.

However, as hydrazine and hydrazinium species penetrate the humic polymers, and are sorbed at binding sites, this sorption will tend to weaken the polymer structure. A gradual loosening of the humate structure will occur, and there will be a gradual increase in the number of sites available for sorption. The contribution of hydrogen bonding to structure stability will be at its greatest in the original hydrogen humate preparation, and analysis of the sorption isotherm using this sorbent does indeed show a gradual increase in the number of binding sites as the extent of interaction increases. An estimate of the differential free energy obtained from the analysis indicates that this also decreases as interaction progresses, which corresponds with the observed steady decrease in the

differential enthalpy of interaction. The observed enthalpy is a net value, and its decrease implies the energy required for structure opening increases as the extent of interaction increased.

The replacement of protons by trivalent aluminium cations as the exchangeable humic cations reduces the contribution of hydrogen bonding to the polymer compaction, but introduces the influence of bridging between carboxylate groups by the metal cations. The strongly polarizing nature of the aluminium ions will result in their solvation shells being strongly held, and may also increase the electrophilic nature of carbon atoms in nearby carbonyl groups, thereby increasing their susceptibility to attack by nucleophilic hydrazine. Indeed the initial differential enthalpy of interaction for the aluminium humate was much greater than for the hydrogen humate, indicating the initial preference of chemisorption in the former case. The observed enthalpy then fell sharply as interaction increased, since the incorporation of hydrazine into aluminium solvation shells will be a less energetic process than exchange of hydrazinium cations for protons in the hydrogen humate case. Whilst the chemisorption process will result in structure weakening, the solvation process may have little effect on the polymer rigidity. This is reflected by the trend in the estimated number of binding sites for the aluminium humate system, which varies sharply at the beginning of interaction, but remains fairly constant as the extent of interaction increased further.

The increase of the differential enthalpy of interaction for the calcium humate system is unusual, but a plot of this enthalpy against the amount of calcium exchanged is linear over most of the interaction. Therefore it appears that the enthalpy of sorption of hydrazine other than by cation exchange is very small, and that sorption by these other mechanisms is favoured initially.

4.2 Vapour Phase

4.2.1 Clay colloids

The First Annual Scientific Report contains results obtained for the sorption of vapour-phase hydrazine and monomethylhydrazine onto sodium-, and iron(III)-exchanged kaolinite, and sodium montmorillonite preparations. The sorption of water vapour by these materials has been examined to appraise the ability of hydrazines to compete with water on the surfaces of undried clays.

The results of water vapour sorption studies are summarized in Table 2, where the parameters (apart from organic matter content) are derived from BET (Brunauer et al., 1967) analyses. The BET theory extends the kinetic theory of adsorption to allow for the condensation of adsorptive at adsorbate sites to give multilayer adsorption. The requirements of BET theory are seldom completely satisfied by real systems. Therefore the values of the derived parameters are useful for comparing the properties of different adsorbents, rather than for unambiguous description. The "C" constant is related exponentially to the first layer heat of adsorption.

The isotherm for sorption onto sodium kaolinite indicates that the sorption process is basically physical, and that the sorbent is macroporous, as would be expected from the packing of the large kaolinite particles. Sorption is initially most likely determined by the hydroxyl groups on the gibbsite-type surface of the kaolinite, rather than by the sodium charge-neutralizing cations.

The low specific surface area and C-content measured for sodium montmorillonite is probably a result of incomplete drying of the clay prior to sorption. The low net energy of sorption of sodium montmorillonite compared to sodium kaolinite may result from the preponderance of siloxane surfaces in this instance as compared to kaolinite where the hydroxyl groups of the gibbsite layer contribute equally to the surface area.

The results for sorption by surface soil clays, which have been treated to remove surface coatings, and those which were not treated, show that the sorption was similar in both cases. The increase in C-constant with depth indicates the presence of more energetic surfaces with relation to water sorption, and in general an increase in surface polar groups.

The differences between the results of the sorption of monomethylhydrazine and of water vapour are summarised in Table 3 (Hayes et al., 1982). Specific surface areas are larger for the monomethylhydrazine sorption, which shows that the hydrazine competed well with water for all sorption sites. The similarity of the net heats of sorption of monomethyl-hydrazine by the two sodium-exchanged clays, compared with the higher value for water vapour sorption onto kaolinite than onto montmorillonite, indicates that hydrazination of the sodium cations may be an important binding mechanism in the former case.

The sorption of monomethylhydrazine onto soil clays is much more energetic than the sorption of water vapour, and the amount of irreversibly held monomethylhydrazine is greatly enhanced by the presence of surface coatings of organic material.

Table 2 Adsorption of water vapour by homoionic clays from deposits
and from different profiles of a tropical soil

Sample	Horizon depth (cm)	Organic matter content (%)	Specific surface area (m²g⁻¹)	C-constant	Net heat of adsorption (kJ mol⁻¹)
Sodium kaolinite	n.a.	None	29	36	-8.9
Sodium montmorillonite	n.a.	None	456	6	-4.6
Soil Clay A	0-20	13.02	103	13	-6.4
Soil Clay A*	0-20	2.14	105	22	-7.6
Soil Clay B	20-50	10.78	70	47	-9.5
Soil Clay B*	20-50	3.06	89	82	-10.9
Soil Clay C	50-90	10.60	49	309	-14.2
Soil Clay C*	50-90	3.99	80	176	-12.8

n.a.   Not applicable

*   Hypochlorite-treated to reduce organic matter content.

TABLE 3.   SORPTION PARAMETERS

	Monomethylhydrazine			Water Vapour		
	[1]NaK	NaM	FeK	NaK	NaM	FeK
BET Analysis:						
C-constant	506	434	33	36	6.4	245
Specific Surface[2] Area ($m^2 g^{-1}$)	36	725	37	29	460	15
Monolayer Capacity (m mol g^{-1})	0.25	2.5	0.25	0.39	1.6	0.21
Net Heat of[3] Adsorption (kJ mol^{-1})	-15.4	-15.1	-8.6	-8.9	-4.6	-13.4
Adsorbate: Exchangeable[4] Metal	3:1	3:1	7:1	6:1	4:1	7:1

[1]
NaK = Sodium-exchanged kaolinite

NaM = Sodium-exchanged montmorillonite

FeK = Iron(III)-exchanged kaolinite

[2] Average error $\pm 8\%$

[3] Average error $\pm 6\%$

[4] To nearest whole numbers

4.2.2 Hydroxy-aluminium montmorillonite

The vapour-phase sorption of hydrazine and monomethylhydrazine onto hydroxy-
aluminium montmorillonite has been studied by equilibrating thin films of the clay
preparation (Section 3.2.3) with the vapour of each hydrazine in a desiccator. Infra-
red spectra of the resulting complexes (Figure 9) show that some of the sorbate is held in
weakly hydrogen bonded, monomeric forms on the clay surface, but that a substantial
part of the sorbate has highly polarized N-H bonds, as a result of hydrazination of
surface sodium ions (Section 4.1.2.2), and because of strong hydrogen bonding to acidic
hydroxyl groups of the aluminium hydroxy polymers:

$$AlOH + N_2H_4 \rightleftharpoons Al\overset{\delta-}{O}\cdots H\cdots\overset{\delta+}{NH_2}.NH_2$$
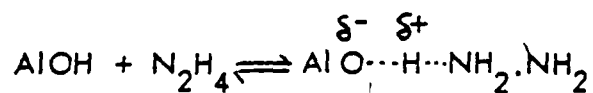
In contrast with the solution phase complexes, very little of the sorbate is fully protonated.
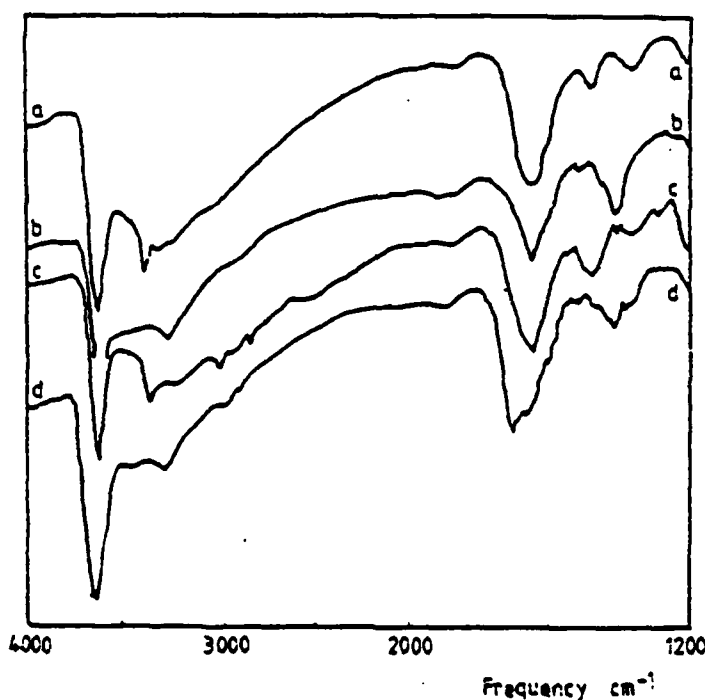

Figure 9. Infra-red spectra of vapour phase complexes:

    a)   hydrazine/hydroxy-aluminium montmorillonite
    b)   as (a), heated at 110°C for 2 days
    c)   monomethylhydrazine/hydroxy-aluminium montmorillonite
    d)   as (c), heated at 110°C for 2 days.

The products of thermal degradation of the vapour phase monomethylhydrazine/clay complex differ from those of the vapour phase hydrazine hydrate/clay complex, and from those of the solution phase complexes of either sorptive. Infra-red spectra of the vapour phase monomethylhydrazine/clay complex show that strong absorptions due to $C=N$ bonds appear when the complexes undergo prolonged heating at 100°C. The formation of such bonds may indicate a degradation process of the type:

$$
\begin{array}{c}
CH_2\!-\!H \\
| \qquad | \\
N\!-\!-\!N\!-\!H \longrightarrow H_2C=NH + NH_3 \\
| \qquad | \\
H \qquad H
\end{array}
$$
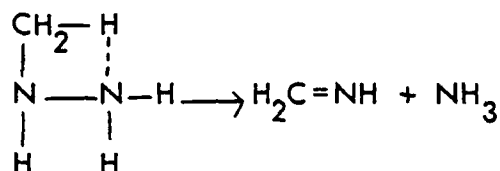
as observed by Golden et al., (1972). This process most likely operates also in the aqueous systems, and in the vapour phase hydrazine hydrate system, but the presence of water molecules there enables the reactive imine groups to react further, forming formaldehyde and further ammonia.

4.2.3 Hydrous oxides

The gravimetric apparatus (Section 3.2.1) used to measure vapour-phase isotherms for the clay colloids has been modified considerably, to improve vacuum and temperature stability. With the refined apparatus it is intended to study in detail the isotherms for hydrazine sorption by goethite preparations, and to analyse the gaseous products of degradation.

Both goethite and iron(III)-exchanged kaolinite samples undergo a colour change during equilibration with monomethylhydrazine vapour. This change is from yellow/brown to black/green, and then back to yellow/brown again on prolonged contact with the vapour. The colour change points to the formation of ferrous iron complexes on the sorbent surfaces. Infra-red spectra of the vapour-phase monomethylhydrazine, or hydrazine, complexes with goethite (Figure 10) do show absorptions in the 1250 and 1150 cm^{-1} positions which can be assigned to NH_2 deformation vibrations of hydrazine directly coordinated to iron on the goethite surface. The intense absorptions at 1620 to 1580 cm^{-1} may arise from hydrazine molecules weakly hydrogen bonded in multilayers on the colloid surface. In this context it is interesting to note that the vapour saturated goethite complexes spontaneously ignite when exposed to air, as the sorbed hydrazines degrade. The spectra also show the presence of a strong 1660 cm^{-1} absorption for the monomethylhydrazine/goethite complex, as seen for similar complexes with hydroxy-aluminium montmorillonite (Section 4.2.2). This points

again to the important role of water in determining reaction pathways for sorbed hydrazines, even though the hydrazines compete well with water for sorption sites.
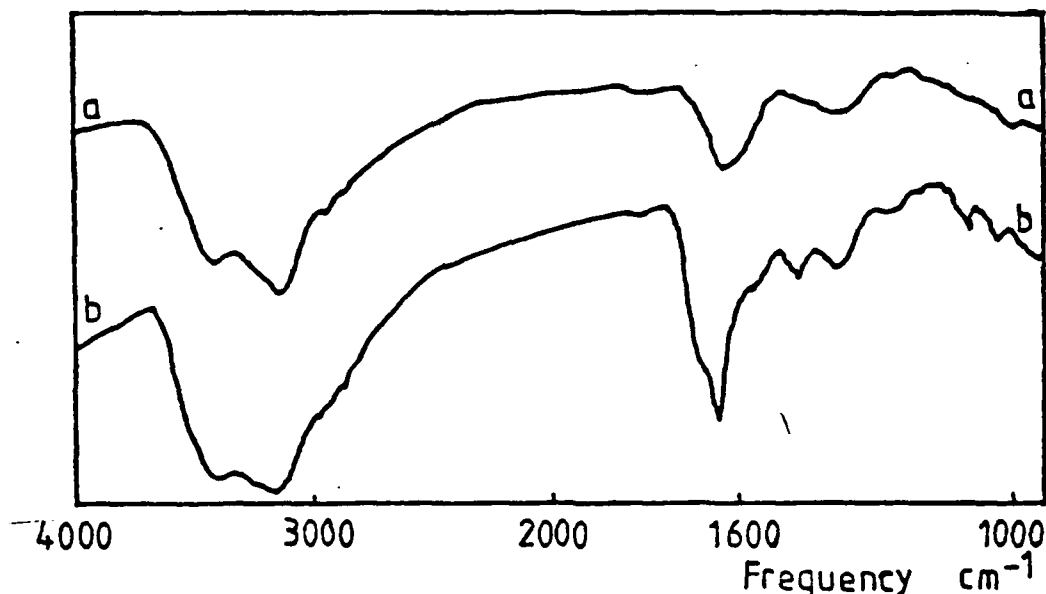

Figure 10. Infra-red spectra of vapour phase complexes:

    a) hydrazine/goethite
    b) monomethylhydrazine/goethite

An isotherm for the sorption of water vapour onto the goethite used in these studies shows the colloid to have a surface area of about $250 \, m^2 g^{-1}$, which is in the range to be expected for preparations synthesized in the manner used in these experiments. A preliminary isotherm for the sorption of monomethylhydrazine vapour onto goethite shows considerable hysteresis, as a result of degradation of the hydrazine.

4.3 Experiments with whole soils

Studies are being carried out with whole soils, to measure their extent of interaction with hydrazine, and to test the effectiveness of treatments to maximise hydrazine degradation.

Three soils are being used which represent a range of soils likely to be encountered, though they necessarily omit some soil types prevalent on the North American landmass. The soils which are used are a clay loam soil (high smectite-type clay mineral content), a loam soil (balanced clay, silt, and sand content, with a good proportion of organic matter), and a sandy loam soil (high sand content brown earth soil, with high iron content). A calcereous soil is also available for further experiments.

TABLE 4

Hydrazine Sorption/Degradation by Whole Soils

SOIL	HYDRAZINE (m mol g^{-1} soil)		
	Water-Desorbable	1 $\underline{M}$ NaCl-Desorbable	Irreversibly sorbed/Degraded
Clay Loam	3.0	5.0	6.5
Loam	3.2	5.5	6.5
Sandy Loam	1.5	1.8	6.1
Cu^{2+}-Clay (N_2)	2.0	3.4	8.7
Cu^{2+}-Clay (Air)	1.8	2.8	23.5

Table 4 contains the results of a number of experiments with these soils. The columns of this table contain, for each soil, the amounts of sorbed hydrazine that is desorbable by water, the amount desorbable by a 1 $\underline{M}$ sodium chloride solution, and the amount of hydrazine unaccounted for in the experiment. This last figure corresponds either to irreversibly sorbed hydrazine, or to degraded hydrazine. All results for the untreated whole soils are for experiments performed in anaerobic systems.

The results show that the presence of a significant amounts of organic matter, or of expanding-lattice clay minerals, increases the amount of hydrazine that can be weakly sorbed by a soil, and increases the amount that can be sorbed as ionic complexes. The amount of hydrazine that can be degraded by the sandy soil appears at first sight to be large, given its lower than average colloid content, but this is a result of the high iron(III) content of this soil.

Two experiments have been performed with the clay loam soil after this has been treated by equilibrating it with 0.5 $\underline{M}$ copper(II) chloride solution, and then flushing excess solution away with distilled water. These copper treated soil preparations show enhanced degradation of hydrazine, particularly using aerated solutions.

The breakdown of soil aggregates is seen to occur in all cases when hydrazine solutions are flushed through the whole soils. Bubbling also occurs in the pore spaces, as a result of hydrazine degradation, and this is particularly vigorous for the copper-treated clay soil.

The results show the very large potential of such soils to interact with hydrazines. The breakdown of soil structure caused by swelling of clays and dissolution of organic matter will have important physical consequences on the fate of hydrazines. The drainage of hydrazines through soils would be greatly impeded by structure breakdown, and in-filling of pores and fissures. Therefore much of the hydrazine would be retained in the upper parts of the surface horizon of a soil, even though this may have been permeable to water.

5. CONCLUSIONS

5.1 The interactions of hydrazines with soil colloids

The results of investigations carried out so far demonstrate that the colloidal components of soil can have a large influence on the fate of hydrazines in the soil environment. This influence arises through two main effects, sorption and degradation. Clay, humic substances, and hydrous oxide colloids can all reversibly sorb hydrazines, and strong, irreversible sorption can occur in some instances. The colloidal components can also catalyse the degradation of sorbed hydrazines, giving rise to four- to five-fold increases in the extents of degradation.

The determining properties in hydrazine sorption are the pH values of the solutions, and the exchangeable metal cations held by the clay and humic colloids, or the metal of the hydrous oxide colloids.

Cation exchange is the main process of interaction with monovalent cation-exchanged colloids, and hence the extent of sorption increases with increasing amounts of protonated hydrazines. Hydrazines are also sorbed by replacing water molecules in the solvation shells of charged species on colloid surfaces.

Aluminium-, iron-, and manganese-exchanged clays have enhanced interactions with hydrazines at high pH values, in conditions where the insoluble metal hydroxides can form on the clay surfaces. Hydrazines are sorbed by the polymeric hydroxide species by strong hydrogen bonding mechanisms. The strength of this bonding destabilizes some of the sorbed hydrazine, which is readily degraded to ammonia on heating the complexes to 110°C.

In the case of iron(III) clays, and also goethite (hydrated iron oxide), interaction is particularly enhanced because of reduction of iron(II), and further complexation of hydrazine with the reduced metal. At high pH values ($>$pH 8) the iron(II) complex formation coats and inactivates goethite surfaces for further sorption. However, the complex is soluble at low pH ($<$ pH 5) and is not retained, even by humic materials.

Hydrazine, being basic, can stimulate the formation of the insoluble hydroxide layers, as is shown by the interaction of hydrazine with aluminium clays. However, the extent of interaction is less than for clays which have been pre-equilibrated at the high pH values.

Hydrazines are chemisorbed by humic substances, especially through reaction with carbonyl groups in the polymers to form Schiff-base type structures. Ion-exchange is an important binding mechanism under acidic conditions (pH 4), but hydrazinium cations can not exchange more polarising cations such as aluminium when these are associated with humic polymers. In this case hydrazination of humic anions is an important binding process. An iron(II)/hydrazine complex formed from iron(III) humate is not retained by the colloids, but some 30% of the original iron(III) is unavailable for reaction.

The particular metal cations held by humic polymers considerably affect the shapes, the dimensions between the "strands", and the solubility of the polymers. Thus, the surface area of humic substances available for interactions with hydrazines, and by inference the penetrability to the internal reaction sites, is strongly influenced by the charge neutralizing exchangeable cation.

Hydrazines are readily sorbed from the vapour phase by clays and hydrous oxides. Both monomethylhydrazine and hydrazine hydrate compete well with water for sorption sites, but the presence of water plays a fundamental role in determining the degradation products of sorbed hydrazines.

The sorption of hydrazines enables soil colloids to exert marked catalytic effects on the degradation of the sorbate in the presence of oxygen at pH values greater than 7.0. The effectiveness of clay colloids in this regard increases with availability of inter-layer surfaces, but the greatest influence is exerted by the metal cation neutralizing the surface charge. Thus hydrated iron oxide (goethite), and iron(III)-exchanged clays have similar catalytic abilities.

Preliminary experiments with whole soils show that they can irreversibly sorb, or degrade, large amounts of hydrazine. The amount of hydrazine degraded is increased up

to greater than 20 mol Kg^{-1} soil for a copper(II) treated, aerated soil. The interactions bring about important physical changes in the soil structure.

5.2 The fate of hydrazine in the soil environment

The fate of hydrazine in a natural soil will be determined by the composition of the soil colloids, by soil aeration, and by the soil solution pH. Treatment of contaminated soils can alter these properties in order to promote the degradation or immobilization of the contaminants.

Lowering the pH of a contaminated soil will minimise hydrazine degradation, and enhance the reversible sorption through cation exchange mechanisms. However, the formation of soluble iron(II)/hydrazine complexes at low pH, and the insolubility of humic colloids, make the lowering of pH of limited usefulness in treating soils.

Hydrazine contamination will raise soil pH. Additional treatments to maintain the elevated pH will maximise:

a) the catalytic degradation effect of soil colloids;
b) the formation of films of aluminium and iron hydrous oxides; these together with _in situ_ hydrous oxides can strongly sorb hydrazines;
c) the penetrability of humic polymers by sorptive.

Metal species that are effective in hydrazine degradation can also be added to the soil. The results of the project so far indicate that copper salts would be highly effective. A water-soluble copper(II) chloride treatment has been tested, and a water-insoluble copper(II) carbonate treatment can also be examined.

Sandy soils have a lower potential for hydrazine degradation and immobilization than other soil types. In such instances the addition of finely-ground smectite clays (preferably Cu^{2+}-, Fe^{3+}-, or Al^{3+}-exchanged), hydrous oxides, or humus would enhance greatly the ability of such soils to degrade hydrazines. Appropriate mechanical disturbance of contaminated soils will, in addition to incorporating treatment amendments, maximise aeration and allow intimate contact to be made between sorptive and soil colloids.

The data obtained with model colloids shows that hydrazine uptake/degradation can be up to 6.4 mol Kg^{-1}, depending on the properties of the colloid. The amounts and properties of soil colloids vary greatly, depending on the soil type. However, even in cases where the colloids comprise only a few percent of the soil components, one hectare of soil ($2 - 2.5 \times 10^6$ kg) will have an enormous capacity to interact with added hydrazines.

6. REFERENCES

von Aebi, H., Dewald, B., and Suter, H. (1965). Autoxydation N^2-substituieter Methylhydrazin: Beeinflussung der Cu- und Fe-Katalyse durch Proteine, Desoxyribonucleinsaure (DNS), und EDTA. Helv. Chim. Acta, 48, (4), 656-674.

Bailey, G.W., White, J.L., and Rothberg, T. (1968). Adsorption of organic herbicides by montmorillonite: Role of pH and chemical character of adsorbate. Soil Sci. Soc. Am. Proc., 32, 222-234.

Belcher, R., and Nutten, A.J. (1970). Quantitative inorganic analysis. Butterworths, London.

Bottomley, F.S. (1970). The reactions of hydrazine with transition metal complexes. Q. Rev. Chem. Soc., 24, 617-638.

Brunauer, S., Copeland, L.E., and Kantro, D.L. (1967). The Langmuir and BET theories. In: Flod, E.A. (Ed.) The solid-gas interface, Vol. 1. Edward Arnold Ltd., London. Marcel Dekker Inc., New York.

Burchill, S., Hayes, M.H.B., Greenland, D.J. (1981). Adsorption of organic molecules. In: Greenland, D.J., and Hayes, M.H.B. (Eds.) The chemistry of soil processes. Wiley-Interscience, New York.

Chia, K.Y., Hayes, M.H.B., and Isaacson, P.J. (1982). Infra-red studies of the interaction of hydrazines with hydroxy-aluminium montmorillonite. In preparation.

Franzen, H., and von Mayer, O. (1908). Über die Hydrazinate einiger Metallsalze. Z. Anorg. Chem., 60, 247-291.

Golden, D.M., Solly, R.K., Gac, N.A., and Benson, S.W. (1972). Very low pressure pyrolysis. VII. The decomposition of methylhydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, and tetramethylhydrazine. Concerted deamination and dehydrogenation of methylhydrazine. Int. J. Chem. Kinetics, 4, 433-448.

Greenland, D.J., and Mott, C.J.B. (1978). Surfaces of soil particles. In: Greenland, D.J., and Hayes, M.H.B. (Eds.), The chemistry of soil constituents. Wiley-Interscience, New York.

Hayes, M.H.B., Isaacson, P.J., Chia, K.Y., and Lees, A.M. (1980). Interactions of hydrazine and of hydrazine derivatives with soil constituents and with soils. First Annual Scientific Report AFOSR-80-0032.

Hayes, M.H.B., Isaacson, P.J., and Yormah, T.B.R. (1982). Vapour phase adsorption and desorption of monomethylhydrazine by homoionic clays. Presented at the 7th International Clay Conference, Pavia (1981). To be submitted for publication in Clays and Clay Minerals.

Heller-Kallai, L., Yariv, S., and Riemer, M. (1973). The formation of hydroxy interlayers in smectites under the influence of organic bases. Clay Minerals, 19, 35-40.

Hinman, R.L. (1958). Base strengths of some alkylhydrazines. J. Org. Chem., 23, (2), 1587-1588.

Isaacson, P.J., and Hayes, M.H.B. (1982). The interaction of hydrazine with hydrogen-, calcium-, and aluminium-humate in aqueous suspension. Submitted to Journal of Soil Science.

Pick, M.E. (1973). The interaction of bipyridylium salts with clay minerals. Ph.D. Thesis, University of Birmingham, U.K.

Shaw, R. (1975). Thermochemistry of hydrazo, azo, and azoxy groups. In: Patai, S. (Ed.). The chemistry of the hydrazo, azo, and azoxy groups. Wiley-Interscience, London.

DATE
ILMED

8